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著者	Katsuno Hiroyasu, Sato Masahide
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Cluster diffusion on two-dimensional surface with immobile impurities

Hiroyasu Katsuno^{a,*}, Masahide Sato^b

^a *Venture Business Laboratory, Nagoya University Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*

^b *Information Media Center, Kanazawa University, Kakuma-cho, Kanazawa 920-1192, Japan*

Abstract

We study diffusion of a two-dimensional cluster on a two-dimensional surface with immobile impurities. We perform a kinetic Monte Carlo simulation using a simple square lattice model. In our model, not only atoms forming an edge of two-dimensional cluster but also atoms in the cluster, which is neighboring impurities in the cluster, are able to evaporate. The cluster diffusion coefficient in the system with a high impurity concentration is larger than that with no impurities.

Keywords: A1. Cluster diffusion, A1. Impurities, A2. Atomic layer epitaxy, A3. Submonolayer

1. Introduction

Foreign substitutional atoms attached on a surface act as trapping centers for adatoms and/or an adsorbate preventing growth of crystal. They also affect behaviors of steps and surface morphology. Theoretically, it has been

*Corresponding author. E-mail address: katsuno@sic.numse.nagoya-u.ac.jp (H. Katsuno). Tel: +81 52 789 3249. Fax: +81 52 789 3248.

predicted that impurities attaching on steps decrease the step velocity and cause morphological instabilities of steps [1–11]. When the period between two impurities is less than the critical nucleus size, the step cannot advance due to the thermodynamic tension which depends on the step curvature.

In a pure system, at least, the two-dimensional cluster diffusion in equilibrium [12–14] and in non-equilibrium [15] is studied. However, to our knowledge there is no study of the cluster diffusion on the surface with impurity while there are many experimental studies of the motion of steps on the dirty surface. The simple understanding for the cluster diffusion on the dirty surface should be established. Thus, in this paper, we focus on the two-dimensional cluster diffusion on a dirty surface, and study the dependence of the cluster diffusion on the impurity density in equilibrium. In Sec. 2, we introduce our simulation model. In Sec. 3, we show the results of the kinetic Monte Carlo simulation of our model, and give brief discussions. In Sec. 4, we summarize our results.

2. Model

Our simulation model is almost the same as that in our previous work [16]. We consider a two-dimensional square lattice with the lattice constant a . The system size is $L_x \times L_y = L^2$ with the periodic boundary condition. We put immobile impurities, which are prohibited from adsorption, evaporation, and diffusion. Then we put a square cluster formed by atoms on the surface. We assume that the bonding energy between an atom and an impurity is zero. The impurities play a role of the obstacle for atoms on the surface and the impurities are strongly bound to the substrate rather than atoms are bound

to the substrate. The model in this paper can be regarded as one component crystal growth system.

The attachment-detachment process is taken account of in our Monte Carlo simulation for simplicity. During Monte Carlo trials, the atoms do not migrate on the surface and they solidify at a vacant site neighboring atoms by impinging. Solid atoms forming the edge of the cluster can evaporate. The frequency of the evaporation of an atom ω_{n_J} depends on the number of bonds parallel to the x - y plane n_J and is expressed as

$$\omega_{n_J} = \omega \exp(-n_J E_J / k_B T), \quad (1)$$

where E_J , k_B , T , and ω represent the bonding energy between nearest neighbor atoms, the Boltzmann constant, temperature, and the frequency of the evaporation of an isolated atom, respectively. We assume $\omega_4 = 0$, that is, the atom with $n_J = 4$ cannot evaporate. When we count n_J , the number of bonds between an atom and an impurity is not counted since the bonding energy is zero.

Hereafter, we focus on the motion of a cluster in equilibrium. In general, the evaporation rate and the impingement rate of atoms are balanced at kink sites, and the total number of atoms is conserved during time evolution. In order to realize the equilibrium state, an atom is forced to impinge immediately at a vacant site neighboring atoms after the evaporation of an atom. In each Monte Carlo trial, the increase of time is given by the inverse of the total transition probability.

In our simulation, for simplicity, immobile impurities are periodically put on the lattice with the concentration c_{imp} . The superlattice of impurities forms a square with a lattice constant $c_{\text{imp}}^{-1/2}$. The initial number of atoms in

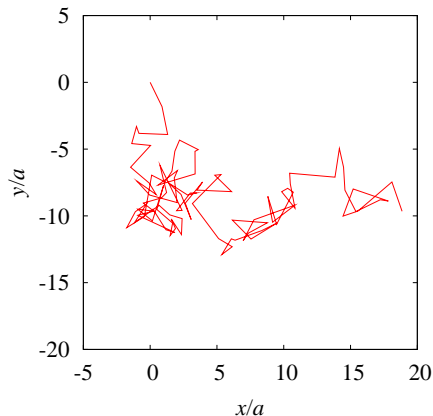


Figure 1: A typical trajectory of a cluster in a pure system.

the cluster is N , which is small enough compared with the system size L^2 . A set of parameters, we use, is as follows: The units of time and length are the frequency of the evaporation of an isolated atom ω , and the lattice constant a , respectively. In this report, we use $\omega = 1$ and $a = 1$. The bonding energy is $\exp(-E_J/k_B T) = 0.1$. Since our model is very simple, it is valid in the low temperature where an atom does not migrate.

3. Results and discussion

Figure 1 shows a typical motion of a cluster position, in which the cluster position is regarded as the cluster center of mass r_{CM} , and Fig. 2 shows a typical form of a cluster at $t = 10^5$ on a pure surface with $c_{\text{imp}} = 0$. We use the coordinate whose origin is the initial position of cluster. In Fig. 1, the cluster size is $N = 900$ and the trajectory with the time upto 10^6 is shown. We find that the cluster moves randomly. During simulation, we sometimes observe that cluster emits small clusters and separates into a few clusters as

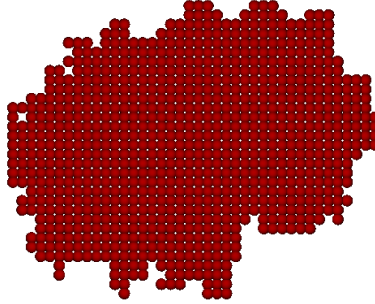


Figure 2: A typical shape of an cluster in a pure system. Filled (red) squares represent atoms.

a result of the evaporation of an atom. In Fig. 2, however, although small vacancies emerge near the step edge, the shape of the cluster keeps compact.

Figure 3 shows a typical trajectory of a cluster on the dirty surface with $c_{\text{imp}}^{-1/2} = 4$ from the starting point (0,0). The cluster position moves at random, which is similar to the cluster motion on the pure surface. Figure 4 shows the cluster shape at $t = 10^5$. Since atoms around impurities are equivalent to the atoms forming the edge of the cluster, the former can evaporate like the latter can. As a result, some vacancies are formed in the cluster although the shape shown in Fig. 4 is almost the same as that in the pure system shown in Fig. 2. Due to evaporation of atoms, it is possible for a cluster to separate into some small clusters. However, as shown in Fig. 4, the cluster size is constant even on the dirty surface with $c_{\text{imp}}^{-1/2} = 4$.

Figures 5 and 6 show the mean square displacement of r_{CM} on a pure surface and surface with $c_{\text{imp}}^{-1/2} = 4$, respectively. The mean-square displacement on the dirty surface increases linearly with increasing time, which is similar

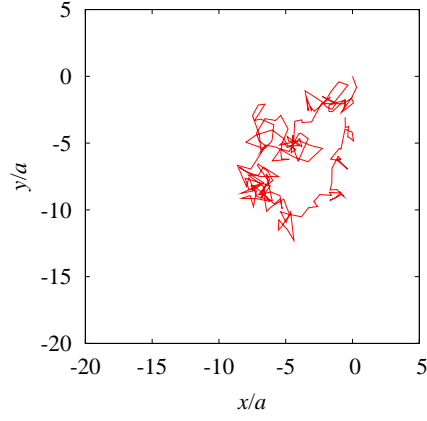


Figure 3: A typical trajectory of an cluster whose size is $N = 900$ and $c_{\text{imp}}^{-1/2} = 4$.

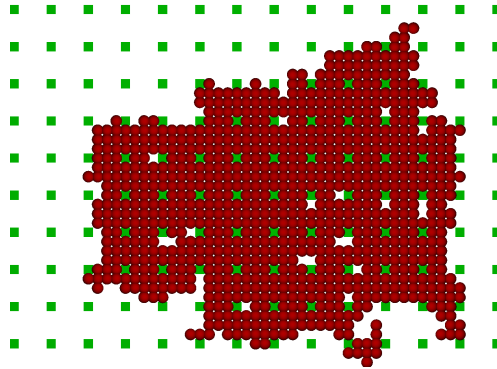


Figure 4: A typical shape of an cluster in a dirty system. Filled (red) squares and filled (green) boxes represent atoms and immobile impurities, respectively.

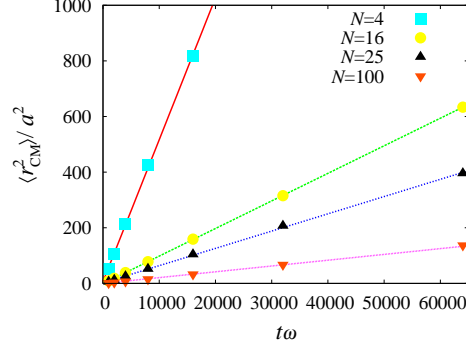


Figure 5: Time dependences of mean-square displacement in a pure system ($c_{\text{imp}}^{-1/2} = \infty$) for various size clusters. t and $\langle r_{\text{CM}}^2 \rangle$ represent the elapsed time in the simulation and the mean-square displacement, respectively. Plotted data of t and $\langle r_{\text{CM}}^2 \rangle$ are scaled by $1/\omega$ and a^2 , respectively.

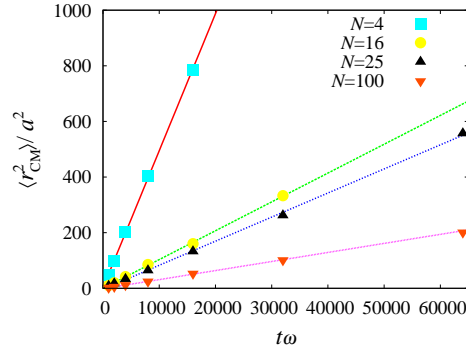


Figure 6: Time dependences of mean-square displacement in a dirty system with $c_{\text{imp}}^{-1/2} = 4$ for various size clusters. t and $\langle r_{\text{CM}}^2 \rangle$ represent the elapsed time in the simulation and the mean-square displacement, respectively. Plotted data of t and $\langle r_{\text{CM}}^2 \rangle$ are scaled by $1/\omega$ and a^2 , respectively.

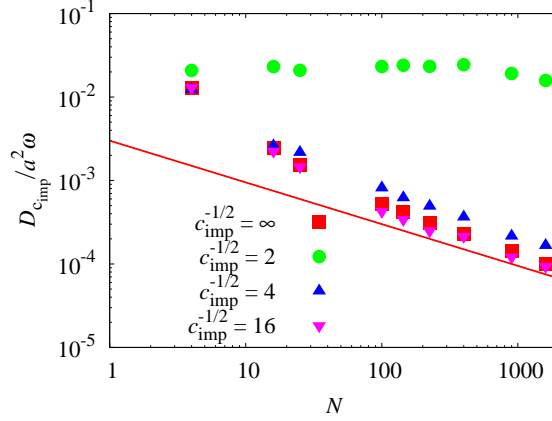


Figure 7: Cluster size dependence of the diffusion coefficient for various impurity intervals. Solid line shows $\sim N^{-1/2}$. Error-bars are less than the size of each symbol.

to that on the pure surface. Using the mean-square displacement $\langle r_{\text{CM}}^2 \rangle$, the diffusion coefficient of a cluster D_{cimp} is expressed as

$$D_{\text{cimp}} = \frac{\langle r_{\text{CM}}^2 \rangle}{4t}, \quad (2)$$

where t represents the elapsed time. We obtain the mean square displacement by averaging over 1000 MC samples, and D_{cimp} is evaluated from Eq. (2). Figure 7 shows the cluster size dependence of D_{cimp} . Except for $c_{\text{imp}}^{-1/2} = 2$, D_{cimp} is proportional to $N^{-1/2}$ when the cluster size N is larger than 100. According to Ref. [12], the size dependence of D_{cimp} is determined by the kinetic processes. When the evaporation and the adsorption of atoms are taken into account, D_{cimp} is proportional to $N^{-1/2}$ [12]. In our simulation, the kinetic processes taken into account are the evaporation and the adsorption of atoms, so that our results with $N > 100$ agrees with the previous analysis [12].

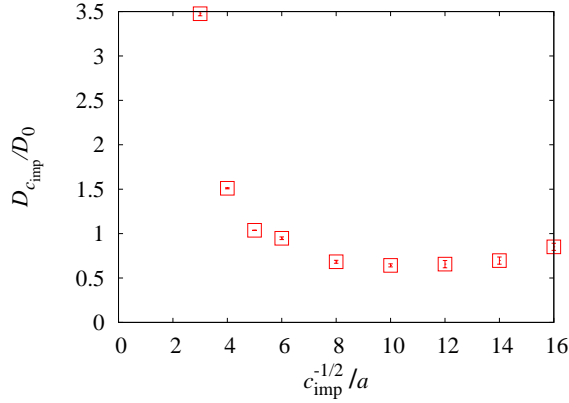


Figure 8: Relative diffusion coefficient for $N = 900$. Error bars show the standard deviation.

From Fig. 7, we find that the cluster size dependence of $D_{c_{\text{imp}}}$ changes with the impurity interval. When $c_{\text{imp}}^{-1/2} = 16$, the impurity interval is large, so that the effect of impurities on $D_{c_{\text{imp}}}$ is small and $D_{c_{\text{imp}}}$ is 0.94 times smaller than that in the pure surface. When $c_{\text{imp}}^{-1/2} = 4$, there are many impurities in the cluster and $D_{c_{\text{imp}}}$ is about 1.5 times larger than that in the pure system. The magnitude of the increment is not negligible. When $c_{\text{imp}}^{-1/2} = 2$, $D_{c_{\text{imp}}}$ is independent of N . The cluster cannot keep its size constant and separate into a few clusters owing to a lot of impurities. For example, when the initial square cluster size is 900, the cluster separates into a few clusters and the maximum cluster size is about 300 in time evolution. For $c_{\text{imp}}^{-1/2} = 2$, the behavior of the cluster is different from that with other impurity interval and out of our focus in this paper, so that in the following analysis, we do not treat cluster behaviors with $c_{\text{imp}}^{-1/2} = 2$.

To investigate the increment of $D_{c_{\text{imp}}}$ caused by the small impurity in-

terval, we introduce the relative diffusion coefficient $D_{c_{\text{imp}}}/D_0$, where D_0 represents the cluster diffusion coefficient in the pure system. Figure 8 shows the impurity interval dependence of the relative diffusion coefficient, in which the cluster size $N = 900$. Error-bars show the standard deviation of data and their values are very small. With the large impurity interval, $D_{c_{\text{imp}}}$ seems to approach D_0 asymptotically. With decreasing the impurity interval, $D_{c_{\text{imp}}}/D_0$ decreases and a minimum of $D_{c_{\text{imp}}}/D_0$ appears at $c_{\text{imp}}^{-1/2} \simeq 10$. Then, $D_{c_{\text{imp}}}/D_0$ increases in the region with a small impurity interval.

When the impurity interval $c_{\text{imp}}^{-1/2} > 10$, the dependence of $D_{c_{\text{imp}}}/D_0$ on $c_{\text{imp}}^{-1/2}$ is explained by pinning of steps caused by impurities. If thermal fluctuations of step are neglected and $c_{\text{imp}}^{-1/2}$ is less than the critical nucleus size, the step cannot advance due to impurities. However, if thermal fluctuations are taken into account, the step occasionally gets over the impurity and moves with a very low velocity. The critical radius is inversely proportional to the supersaturation. In our model, the critical radius is infinite because the system is in equilibrium. Thus, irrespective of $c_{\text{imp}}^{-1/2}$ the migration of a cluster on a dirty surface becomes slower than that on a pure surface. The effect of impurities decreases with increasing the distance between impurities, and we expect that $D_{c_{\text{imp}}}$ approach to D_0 with a very low impurity density, which agrees with our results.

When $c_{\text{imp}}^{-2} < 10$, the diffusion coefficient of the cluster decreases with increasing $c_{\text{imp}}^{-1/2}$. This result conflicts with the effect of the pinning by impurities, so that other different mechanisms seem to be effective. In our model, atoms need to evaporate from a cluster for the cluster moving. In the pure system, evaporation occurs only at the cluster edge sites. On the other hand,

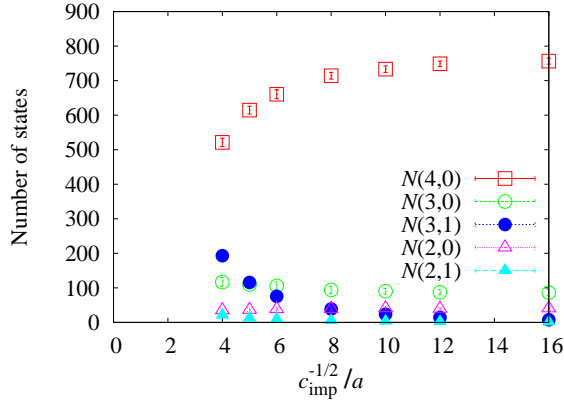


Figure 9: Impurity interval dependences of the number of state. The cluster size is $N = 900$.

in the dirty system, in addition to the evaporation of atoms from the cluster edge site, atoms around impurities can evaporate. This effect probably contribute the enhancement of the cluster diffusion.

In order to investigate the enhancement of the diffusion coefficient with small $c_{\text{imp}}^{-1/2}$, the number of atoms $N(i, j)$ is introduced. A set of (i, j) shows a state of an atom: i and j represent the number of neighboring atoms and impurities, respectively. The indexes i and j are restricted to satisfy $i + j \leq 4$ due to the lattice symmetry. As each immobile impurity is isolated with a regular spacing, small cluster of impurities are not formed, that is, $N(i, 2) = N(i, 3) = N(i, 4) = 0$. $N(i, 0)$ is the number of atoms, which do not attach impurities: $N(4, 0)$ represents the number of atoms in bulk, $N(3, 0)$ is the number of atoms at the step edge position, and $N(2, 0)$ is the number of atoms at the kink. $N(i, 1)$ is the number of atoms which attach to one impurity: $N(3, 1)$ is the number of atoms in bulk with neighboring an

impurity, and $N(2, 1)$ is that of atoms attaching two atoms and one impurity. The dependences of $N(i, 0)$ and $N(i, 1)$ on various $c_{\text{imp}}^{-1/2}$ are shown in Fig. 9. The size of cluster is $N = 900$. To avoid the effect of the initial condition, the time average of the number of states is carried out after $t > 10^4$. When the interval $c_{\text{imp}}^{-1/2} = 16$, the interval is so long that the effect of impurities are small. The numbers of states are almost the same as those in the pure system. Although we do not show the results in Fig. 9, $\langle N(3, 0) + N(2, 0) \rangle$ and $\langle N(4, 0) \rangle$ in the pure system are estimated to 122 and 770, respectively. These values are reasonable because the shape of the cluster is roughly square in our simulation as shown in Figs. 1 and 3. When there are impurities on the surface, $N(3, 1)$ increases and $N(4, 0)$ decreases with decreasing the impurity interval, but $N(3, 0)$, $N(2, 0)$ and $N(2, 1)$ hardly change.

We focus on the drastic increment of $N(3, 1)$ in order to estimate the critical impurity interval which gives the minimum value of $D_{c_{\text{imp}}}/D_0$. When impurities exist in the cluster, the evaporation of atoms which attach to impurities becomes possible. The evaporation from the inside of the cluster enhances the cluster diffusion. As shown in Fig. 9, $N(3, 1)$ is always larger than $N(2, 1)$, so that we predict that $N(3, 1)$ is more important than $N(2, 1)$ with regard to the enhancement of $D_{c_{\text{imp}}}$. In the pure surface, D_0 is mainly determined by $N(3, 0)$. On the other hand, in the system with impurities, the contribution of $N(3, 1)$ to the enhancement of $D_{c_{\text{imp}}}$ should be also taken into account because the state of $N(3, 1)$ is energetically the same as that of $N(3, 0)$, which implies that the evaporation frequency of the atom of $N(3, 1)$ is the same as that of $N(3, 0)$. When $N(3, 1) \simeq N(3, 0)$, the effect of the evaporation of atoms attaching impurities is not probably negligible. $N(3, 1)$

roughly represents the number of atoms around impurities in the cluster and is approximately given by

$$N(3, 1) \simeq 4Nc_{\text{imp}}. \quad (3)$$

During simulation, the shape of cluster is roughly square, so that $N(3, 0)$ is roughly estimated by

$$N(3, 0) \simeq 4\sqrt{N}. \quad (4)$$

Thus, the critical impurity concentration is given by

$$c_{\text{imp}}^* \simeq \frac{1}{\sqrt{N}}, \quad (5)$$

that is, the critical impurity interval is

$$c_{\text{imp}}^{*-1/2} \simeq N^{1/4}. \quad (6)$$

For $N = 900$, the critical impurity interval is obtained as 5.5. In Fig. 8, the relative diffusion coefficient has a minimum point at around $c_{\text{imp}}^{-1/2} = 10$. In spite of the rough estimation, $c_{\text{imp}}^{*-1/2}$ given by Eq. (6) is of the same order of the results of simulation, so that our scenario is probably good explanation for the dependence of the relative diffusion coefficient on the interval between impurities.

4. Summary

We focused the two-dimensional cluster diffusion on the dirty surface. The simple square lattice model was introduced and kinetic Monte Carlo simulation of the model was performed in equilibrium. In the pure system,

it is conformed that the cluster diffusion is described as the picture of the long wavelength analysis on the Langevin dynamics[12] in the cluster size $N > 100$. With the immobile impurities, the large impurity interval prevents the step advancing due to the infinity of the critical radius. The cluster diffusion coefficient is smaller than that in the pure system. The small impurity interval increases the number of the impurity in the cluster. Impurities in the cluster provides the increase of the evaporation atom from inside the cluster, and we detect that the cluster diffusion coefficient is larger than that in the pure system. The increase of the cluster diffusion coefficient is effective when the number of atoms neighboring the impurity in the cluster is larger than that of the step atom. The fluctuation of the step motion is enhanced by the evaporation of atoms not only from the step but also from inside the cluster.

In this paper, we only studied the island diffusion in one of the simple situations. Now we intend to study the effect of random distribution of impurities and another process such as the diffusion of atoms.

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